

GRINBERG, A. A.

SOV/62-58-8-22/22

AUTHOR: None Given

TITLE: The General Meeting of the Department of Chemical Sciences of the AS USSR From April 24 to 25, 1958 (Obshcheye sobraniye otdeleniya khimicheskikh nauk AN SSSR ot 24-25 aprelya 1958 g.)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 8, pp. 1017 - 1018 (USSR)

ABSTRACT: At this General Meeting the following scientists delivered lectures: The Corresponding Members, Academy of Sciences, USSR, A. A. Grinberg, I. A. Kazarnovskiy, A. D. Petrov, and R. Kh. Freydlina, Doctor of Chemical Sciences. A. A. Grinberg reported on the new knowledge on the kinetics and the mechanism of the reactions of the exchange and the substitution in complex compounds of platinum. Based on experimental data the lecturer concluded that in the process of the isotopic exchange in the derivatives of bivalent palladium the dissociation and association mechanism play an important role. These explanations raised a vivid discussion in which mainly I. I. Chernyshev, Member, Academy of Sciences, USSR and the Corresponding Members, Academy of Sciences, USSR V. I. Spitsina, Ya. K. Syrkin, I. V. Tananayev, and A. D. Gelman, Doctor of Chemical Sciences took part. I. A.

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The General Meeting of the Department of Chemical Sciences of the AS USSR  
From April 24 to 25, 1958

Kazarnovskiy held a lecture on the investigations of the kinetics and the mechanism of the arbitrary decomposition of potassium ozonide (employing the magnetic method) carried out by himself and his collaborators (S. I. Reykhshteyn and L. N. Bykova, Candidates of Chemical Sciences). A. D. Petrov on behalf of the collaborators of the Institute of Organic Chemistry (V. F. Mironov, V. A. Ponomarenko, S. I. Sadykh-Zade and Ye. A. Chernyshev) reported on "The Synthesis of New Forms of Silicon Containing Monomers". He announced new results of investigations of the catalytic binding of hydride silanes with unsaturated and aromatic compounds not published up to now. In the discussion following this lecture V. V. Kershak, Corresponding Member, Academy of Sciences, USSR, said that the results obtained by the team of A. D. Petrov were of great importance. The corresponding conclusions had to be drawn from the influence exerted by silicon in the various groups on the reactivity of these compounds. The report delivered by R. Kh. Freydlina on "The Homolytic Isomerization in Solutions" raised great interest. This lecture was followed by a vivid exchange

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The General Meeting of the Department of Chemical Sciences of the AS USSR  
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of opinions in which mainly the following Members, Academy of Sciences, USSR took part: I. L. Knunyants, A. N. Nesmeyanov, and N. N. Semenov, as well as the Corresponding Members, Academy of Sciences, USSR V. V. Nekrasov, Ya.K. Syrkin and A. D. Petrov. I. L. Knunyants said that the work carried out by R. Kh. Freydlina on the homolytic isomerization in solutions represented an important event in organic chemistry.

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IN'KOVA, Ye.N.; GRINBERG, A.A.

Reduction of platinum occurring in the course of the synthesis of  
hexamine. Trudy LTI no.46:17-20 '58. (MIRA 14:4)  
(Platinum) (Diphenylamine)

GRINBERG, A.A.

"Mutual Interaction of Platinum Complexes."

a paper presented the London International Conference on Coordination  
Chemistry London, 6-11 apr '59

SO: B-3,129,763

8 May '59

GRINBERG, A.A.; SHAGISULTANOVA, G.A.

Investigating the kinetics of bromine isotope exchange in potassium platinum tribromotriamine. Radiokhimiia 1 no.1:91-102 '59.  
(MIRA 12:4)

(Bromine--Isotopes)

(Platinum compounds)

GRINBERG, A.A.; IN'KOVA, Ye.N.

Exchange of ethylamine in the system  $[\text{Pt}(\text{CH}_3\text{CH}_2\text{NH}_2)_4]\text{SO}_4 - 4\text{CH}_3\text{C}^{14}\text{H}_2$   
NH<sub>2</sub>. Radiokhimiia 1 no.1:103-104 '59. (MIRA 12:4)  
(Platinum compounds) (Carbon—Isotopes)  
(Ethylamine)

GRINBERG, A.A.; PETRZHAK, G.I.; YEVTEYEV, L.I.

Preparation and properties of uranium oxalic acid salts of rare  
earth elements. Radiokhimiya 1 no.3:300-308 '59.

(MIRA 12:10)

(Oxalic acid) (Oxalatouranates)



SOV/78-4-1-16/48

5(2)

AUTHORS:

Grinberg, A. A., Itskovich, T. B., Troitskaya, A. D.

TITLE:

On the Question of the Structure of Phosphorous Acid and Its Derivatives (K voprosu o stroenii fosforistoy kisloty i yeye proizvodnykh)

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 1, pp 79-81 (USSR)

ABSTRACT:

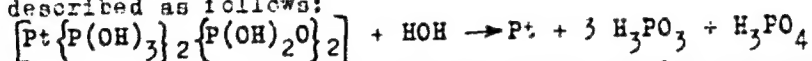
The reciprocal effect between an aqueous solution of potassium chloroplatinate, trimethyl phosphite and dimethyl phosphorous acid was investigated. The experimental data on the saponification process of dimethyl phosphorous acid and its complexes were found by measuring the change of the pH value. Equal concentrations of aqueous solutions of dimethyl phosphorous acid and  $[Pt\{P(OCH_3)_2OH\}_2\{P(OCH_3)_2O\}_2]$  were heated in a water bath at  $100^\circ$ . After a certain time the pH value was measured at  $20^\circ$  in order to find out the difference of saponification between free dimethyl phosphorous acid and the acid coordinatively bound with bivalent platinum as an addendum. It is evident from the change of the pH value on heating that

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On the Question of the Structure of Phosphorous Acid and Its Derivatives

free dimethyl phosphorous acid saponifies quicker during the first 15 minutes with a considerable reduction of the pH value of the solution. The saponification of group  $P(OCH_3)_2OH$  in the complex  $[Pt\{P(OCH_3)_2OH\}_2\{P(OCH_3)_2O\}_2]$  is insignificant. The qualitative and quantitative determination of the final products of the platinum complex saponification showed platinum, phosphorous and phosphoric acid. The saponification process is described as follows:



The experiments prove that in platinum complex compounds the addenda of dimethyl phosphorous acids and phosphorous acid contain trivalent phosphorus. There are 1 figure, 2 tables, and 9 references, 7 of which are Soviet.

SUBMITTED: October 26, 1957

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SOV/78-4-2-11/40

5(2)

AUTHORS:

Grinberg, A. A., Chapurskiy, I. N.

TITLE:

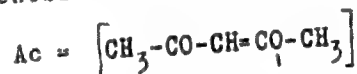
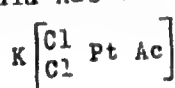
Acetyl Acetonates of Bivalent Platinum (Atsetilatsetonaty dvukhvalentnoy platin.)

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 2, pp 314-318 (USSR)

ABSTRACT:

The orange and light yellow acetyl acetonates of bivalent platinum, which are soluble in water, and the cal.ry-yellow acetyl acetonates, which are insoluble in water, were investigated with regard to their production conditions and physico-chemical properties. The orange salt is easily soluble in water (~4.73% at 15°), difficultly soluble in alcohol and practically insoluble in ether, chloroform, and benzene. The formula by Werner was proved by the analyses of this salt (Ref 3). On account of the determination of the molecular electric conductivity the following coordination formula has been suggested for the orange salt:



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Acetyl Acetonates of Bivalent Platinum

The formula of the light yellow salt is:  $K \begin{bmatrix} Cl \\ Ac \end{bmatrix} Pt Ac$

The light yellow salt is also easily soluble in water and difficultly soluble in alcohol. The solubility in water is ~10.2%. If hydrochloric acid is added, an amorphous yellow precipitate separates out of the aqueous solutions of this salt. It is difficultly soluble in water and easily soluble in organic solvents. The canary-yellow acetyl acetonate is insoluble in water but easily soluble in organic solvents, as benzene, alcohol, chloroform, and carbon tetrachloride. By analyzing this compound the following formula was found:  $Pt(C_5H_7O_2)_2$ . The molecular weight of this compound is 388 (calculated 393.34). The solubility determination of  $Pt(C_5H_7O_2)_2$  in benzene and alcohol at 25° showed the following results:  $L_{25^\circ}$  in ethyl alcohol =  $6.5 \cdot 10^{-3}$  g-mol/l,  $L_{25^\circ}$  in benzene =  $4 \cdot 10^{-2}$  g-mol/l.

The determination of the molecular electric conductivity of the weak aqueous solutions shows that the yellow salt and the orange salt are binary electrolytes whereas the insoluble

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SOV/78-4-2-11/40

Acetyl Acetonates of Bivalent Platinum

platinum diacetyl acetonate is no electrolyte. There are  
1 table and 4 references, 3 of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskii institut im. Lensovet  
(Leningrad Technological Institute imeni Lensovet)

SUBMITTED: November 3, 1957

Card 3/3

5(4)

SOV/78-4-2-12/40

AUTHORS: Grinberg, A. A., Kukushkin, Yu. N.

TITLE: On the Kinetics of the Interaction of Ammonia With Several Salts of the Type  $K_2[PtX_4]$  and  $K[PtNH_3X_3]$  (O kinetike vzaimodeystviya ammiaka s nekotorymi solyami tipa  $K_2[PtX_4]$  i  $K[PtNH_3X_3]$ )

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 2, pp 319-324 (USSR)

ABSTRACT: The interaction of ammonia with the salts  $K_2[PtCl_4]$ ,  $K[PtNH_3Cl_3]$ ,  $K_2[PtBr_4]$ , and  $K[PtNH_3Br_3]$  was examined in various concentrations and at various temperatures. It was found that the reaction rate of the interaction depends on the concentration of ammonia and the complex salts. The kinetic data on the interactions in the systems  $K_2[PtCl_4]-2NH_3$  and  $K[PtNH_3Cl_3]-NH_3$  are shown in tables 1 and 2. The results show that the ammonia molecule in the complex compound  $K[PtNH_3X_3]$  ( $X=Cl, Br$ ) considerably increases the mobility of the addenda which are in cis-position to ammonia.

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On the Kinetics of the Interaction of Ammonia With Several Salts of the  
Type  $K_2[PtX_4]$  and  $K[PtNH_3X_3]$

This cis-influence of the ammonia molecule on the reactivity is stronger at the coordinate  $Br-Pt^{II}-Br$  than in the chlorine system  $Cl-Pt^{II}-Cl$ . The activation energy in the system  $K_2[PtBr_4] \cdot 2NH_3$  is somewhat higher than in the respective chlorine system. There are 4 figures, 5 tables, and 5 references, 3 of which are Soviet.

SUBMITTED: November 22, 1957

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5(4)  
AUTHORS: Grinberg, A. A., Vrublevskaya, L. V., Gil'dengershel', Kh. I.,  
Stetsenko, A. I. SOV/78-4-5-13/46

TITLE: New Data Concerning the Acid-basic Properties of Complex Compounds (Novyye dannyye po kislотно-osnovnym svoystvam kompleksnykh soyedineniy)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4; Nr 5,  
pp 1018-1027 (USSR)

ABSTRACT: The present paper was submitted at the VII All-Union Conference on the Chemistry of Complex Compounds at Leningrad on October 11, 1956. The behavior of acid-basic complex compounds and the solvation equilibria in aqueous solutions of ammoniacates and amines of metal was investigated. The acid properties of the propylene-diammine-derivatives of quadrivalent platinum as well as the acid properties of cis-Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> were investigated. The cis-isomer of the propylene-diammine-derivative Pt<sup>4+</sup> was for the first time synthesized. The acid properties of this compound were determined by

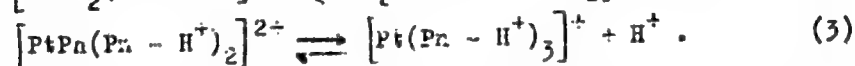
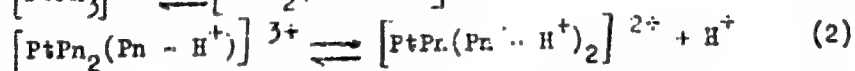
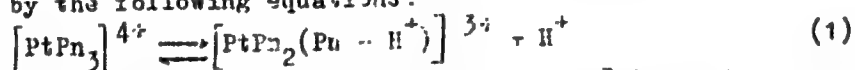
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SOV/78-4.5.13/46

New Data Concerning the Acid-Basic Properties of Complex Compounds

potentiometric titration by means of the glass electrode. Figure 1 shows the titration curve of  $[\text{PtPn}_3]\text{Cl}_4$  with NaOH. The process of the acid dissociation of  $[\text{PtPn}_3]^{4+}$  is described by the following equations:



It was shown that the cis-isomer is a dibasic acid with the following dissociation constants:  $K_1 = 6.1 \cdot 10^{-9}$  and

$K_2 = 4.4 \cdot 10^{-11}$ . The trans-isomer is a weak monobasic acid,

$K_1 = 1.8 \cdot 10^{-11}$ . The potentiometric titration of the isomeric

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compound  $[\text{PtPn}_2\text{Cl}_2]\text{Cl}_2$  was investigated. The dissociation

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New Data Concerning the Acid-basic Properties of Complex Compounds

constants of this compound are the following:  $K_1 = 4.3 \cdot 10^{-10}$  and  $K_2 = 4.9 \cdot 10^{-11}$ . The acid properties of the cis-isomers of the propylene-diammine-cycle are more marked than those of the corresponding ammine derivatives.  $[\text{Pt}(\text{N}_3)_2]\text{Cl}_4$  is a tri-basic acid. The constants of the stepwise dissociation are the following:  $3.9 \cdot 10^{-6}$ ;  $2.5 \cdot 10^{-10}$  and  $2.1 \cdot 10^{-11}$ . The acid properties of the following preparations were investigated:  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ;  $[\text{Co}(\text{N}_3)_2]\text{J}_3$ ;  $[\text{I}(\text{N}_3)_2]\text{J}_3$ ;  $[\text{Rh}(\text{N}_3)_2]\text{J}_3$ . The titration curves of this compound are shown by figures 4 and 5. The causes of the cis-effect and of the acidity of the propylene-diammine-derivatives of quadrivalent platinum are discussed. On the basis of experimental data the stepwise dissociation of  $\text{Pt}(\text{Thio})_4(\text{OH})_2$  ( $\text{Thio} = \text{SC}(\text{NH}_2)_2$ ) is calculated. The constants  $K_1$  and  $K_2$  are approximately  $10^{-5} - 10^{-6}$  and  $10^{-9} - 10^{-10}$  respectively. There are 5 figures and 26 references, 11 of which are Soviet.

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SOV/78-4-7-2/44

5(2)

AUTHOR:

Grinberg, A. A.

TITLE:

On Research Work of Actual Interest in the Field of Inorganic Chemistry (Ob aktual'nykh napravleniyakh issledovaniy v oblasti neorganicheskoy khimii)

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 7, pp 1475-1480 (USSR)

ABSTRACT:

This lecture was delivered on September 8, 1958 at the Slovakian Academy of Sciences at Bratislava. As the most important field of research the author mentions: transuranium, the elements of rare earths and rare elements (yttrium, lanthanum, cerium, zirconium, niobium, molybdenum, ruthenium, etc. play a part in the chemistry of nuclear reactors, germanium, titanium, beryllium have become technically interesting, lithium, uranium, deuterium, and cadmium are also of importance for nuclear power engineering). Mention is further made of the intensification of reactions by catalysis, works on "anomalous" valences, the investigation of complex compounds, development of the chemistry of complexons (on the basis of the works by Professor Příbyl et al.), the chemistry of internal complex

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SOV/78-4-7-2/44

On Research Work of Actual Interest in the Field of Inorganic Chemistry

salts, and synthesis and the application of specific ion exchangers. Mention is further made of the new development of the chemistry of hydrides (Al-H-compounds, gallium-hydrogen compounds). The chemistry of polymers is of importance also in inorganic chemistry: aluminum silicates, metaphosphates. Furthermore, problems of the structure and the isomeric states of simple and inorganic acids remain to be explained. The chemistry of intermetallic compounds requires new fundamental bases for the classification of accumulated data. N. S. Kurnakov dealt with compounds of reciprocal composition. The investigation of phases of varying composition, the mixed crystals and isomorphous mixtures belong to the field of general chemistry, which are of importance for theoretical and applied radiation chemistry, geochemistry, and crystallochemistry. Besides work connected with the structure of solid phases, work concerning non-aqueous solvents is of growing practical and theoretical interest.

SUBMITTED: December 25, 1958

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5(2)

SOV/78-4-7-10/44

AUTHOR: Grinberg, A. A.

TITLE: New Data on the Kinetics of Substitution Reactions and the Reciprocal Influence of Coordinated Groups (Novyye dannyye po kinetike reaktsiy zameshcheniya i po vzaimnomu vliyaniyu koordinirovannykh grupp)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 7, pp 1517-1532 (USSR)

ABSTRACT: The author gives a survey of papers available so far, which deal with the trans-effect discovered by I. I. Chernyayev, and he gives the results obtained for the reactions of Pt<sup>II</sup> and Pt<sup>IV</sup> in tables 1 and 2. In collaboration with S. S. Borzakova, Ye. N. In'kova, N. V. Kiseleva, Yu. N. Kukushkin and G. A. Shagisultanova, compounds of the type K<sub>2</sub>PtX<sub>4</sub> and K<sub>2</sub>PdX<sub>4</sub> (X = halogen) were investigated kinetically, spectrometrically, and potentiometrically, and pH and electric conductivity were measured (Figs 1-4). Whereas the reactions in the platinum system are reversible, the palladium system undergoes irreversible transformations (Fig 5), which lead to ions with a coordination number > 4, probably PdCl<sub>5</sub><sup>3-</sup> or PdCl<sub>6</sub><sup>4-</sup> (Figs 6,7).

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New Data on the Kinetics of Substitution Reactions and the Reciprocal Influence of Coordinated Groups

Further, investigations were carried out of the kinetics of the reactions of  $K_2[PtCl_4]$ ,  $K[PtNH_3Cl_3]$ ,  $[Pt(NH_3)_3Cl]Cl$  and  $K_2[PtBr_4]$  with alkalis, of the same compounds and  $K[PtPyCl_3]$ ,  $K[PtNH_3Br_3]$  (Py = pyridine) with ammonia, and of  $K_2[PtCl_4]$ ,  $K[PtNH_3Cl_3]$  and  $K[PtPyCl_3]$  with pyridine. The coefficients of the rate of substitution reactions are given in table 3, the kinetic characteristic values of the substitution reactions at different temperatures by table 4. The author arrives at the following conclusions: The previously found reverse ratio between the thermodynamical stability of some compounds of  $Pt^{II}$  and their kinetic lability applies also to reactions with water and ammonia. To the thermodynamical characteristic values and the instability constant it is necessary to add kinetic characteristic values as e.g. the velocity (or half-life period) of the establishment of the solution equilibrium. On the basis of the new data on the exchange of substituents in symmetric complexes of  $Pt^{II}$ , which contain thiourea or ethylamine, a rapid

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New Data on the Kinetics of Substitution Reactions and the Reciprocal Influence of Coordinated Groups

reaction rate of the  $Pt^{II}$ -compounds with such substituents as tertiary phosphines, esters of phosphoric acid, and thioesters may be assumed to develop according to the parallelism existing between the exchange velocity of the addend and the trans-effect. The data obtained for the reactions with  $NH_3$  and pyridine indicate the existence of an intermolecular cis-effect, which manifests itself by increased mobility and reactivity of the halogen atoms, which are in cis-position with respect to  $NH_3$  of Py. The author sets up the following hypothesis in this connection: If the interior range contains several groups pre-tending to a reaction with the free valence electrons of  $Pt^{II}$ , the degree of the reaction of each of these groups becomes lower than if such neighboring groups are lacking. On the other hand, the existence of such groups which show no or only little reaction with the valence electrons of  $Pt^{II}$ , must increase the trans-effect of the addends. The cis-effects thus manifest themselves by an increase or attenuation of the trans-effects. The influence of light upon the reactions observed by other authors (Refs 29,39,40,41) must be further investigated for various wave lengths and by the use of catalysts. On the basis of the

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SOV/78-4-7-10/44

New Data on the Kinetics of Substitution Reactions and the Reciprocal Influence of Coordinated Groups

papers of references 43 and 44 the possibilities of trans-effects must be investigated also in the complex compounds of other metals (as e.g. cobalt). There are 11 figures, 4 tables, and 44 references, 27 of which are Soviet.

SUBMITTED: December 26, 1958

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GRINBERG, A.

New information on the kinetics of substitution reactions and the mutual effect of the coordinated groups. Tr. from the Russians. p. 201.

CHEMICKÉ ZVESTI. Bratislava, Czechoslovakia. Vol. 13, No. 4, Apr. 1959.

Monthly list of East European Accessions (EEAI) LC, Vol. 8 No. 10  
Oct. 1959.  
Uncl.

S/186/CO/002/001/013/022  
A057/A129

AUTHORS: Grinberg, A.A.; Trofimov, A.M.; Stepanova, L.N.  
TITLE: Determination of the charge of polynuclear complex ruthenium ions by the ion-exchange method

PERIODICAL: Radiokhimiya, v. 2, no. 1, 1960, 78 - 82

TEXT: The present investigation was carried out after a visit of one of the present authors in the laboratory of J.M. Fletcher in Harwell (England) in connection with some new data (reported by Fletcher et al. at the International Conference on Coordination Chemistry, London, May 6, 1959, under the title: binuclear chloro and other polynuclear complexes of ruthenium) concerning ruthenium complexes. In the discussion the investigators stated the importance of direct determination of the charge of the red polynuclear ruthenium cation, for which the British chemists assumed a charge of +6. Definite solution of this question was of interest apart from the verification of data obtained by Fletcher et al., because complex anions with charges greater than four are rare. F.M. Jaeger and P. Koets [Ref. 3: Z. anorg. Ch., 170, 347 (1928)] reported about nine-valent cations, but their existence is at present in question [J.C. Bailar, Ref. 4: Chem-

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S/186/60/002/001/013/022  
A057/A:29

Determination of the charge of polynuclear....

istry of the Coordination Compounds, 65, N.Y. (1956)]. Hence it was important to discover a method to determine the charge of highly-charged cations. Thus the present authors investigated the applicability of the recently published ion-exchange method [A.V. Trofimov and L.N. Stepanova, Ref. 2: Radiokhimiya, 1, 4, 403 (1959)] to the determination of the charge of the red polynuclear ruthenium cation. In further investigations this method will be applied to check data obtained by Jaeger and Koets. In the present experiments a sample of the ruthenium complex synthesized by Fletcher et al. was used. The principle of the ion-exchange method consists in the determination of the distribution coefficient  $\alpha$  of radioisotopes on two ion-exchange resins with different swelling capacities. According to the rules of ion-exchange: 
$$\lg \frac{a^I}{a^{II}} = \frac{z_1}{z_2} \lg \frac{C^I}{C^{II}} + \frac{z_1 - z_2}{z_2} \lg \frac{V^{II}}{V^I} \quad (1)$$

I and II refer to the resins with two swelling capacities,  $z_1$  - effective charge of the investigated ions;  $z_2$  - charge of the exchanged ions,  $C^I$  and  $C^{II}$  equivalent exchange capacity of the resins (per 1 g of dry resin),  $V^I$  and  $V^{II}$  - specific volumes of swollen resins under the conditions of the distribution coefficient determination. In the exchange of mono-valent ions ( $H^+$ ,  $Na^+$  etc.), the charge can be calculated by:

$$z = \frac{\lg \frac{a^I}{a^{II}} + \lg \frac{V^{II}}{V^I}}{\lg \frac{C^I}{C^{II}} + \lg \frac{V^{II}}{V^I}} \quad (2)$$

and if the equivalent exchange capacities of the two resins are the same: 
$$z = \frac{\lg \frac{a^I}{a^{II}}}{\lg \frac{V^{II}}{V^I}} + 1 \quad (3)$$

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A057/A129

# Determination of the charge of polynuclear....

The experimental determination of  $\alpha$  as well as of the specific volumes of the swollen ion-exchange resin must be carried out under the same conditions. The investigated element must be ions. The ion-exchange must be strictly reversible and the complexes must be stable. According to Ye.I. Il'yenko, B.P. Nikol'skiy and A.M. Trofimov [Ref. 5: Tr. komissii po analiticheskoy khimii (Proceedings of the commission for analytical chemistry), Izd. AN SSSR (Ed. AS USSR), 9 (12), 148 (1958)] reversibility is not always maintained in exchange of ruthenium complexes. The present authors demonstrated in corresponding experiments that by adding  $\text{HNO}_3$  solution the red complex changes into a yellow complex, thus exchange using  $\text{H}^+$  ions cannot be carried out. It was observed that in  $\text{NaNO}_3$  solutions the complex is stable, and is strongly adsorbed on sulfonated KY-2 (KU-2) cation exchange resin. About 50% of the red complex is adsorbed from 3.5 N  $\text{NaNO}_3$  solution. Solutions containing between 0.5 and 5 mg/l ruthenium obey Beer's law with an absorption maximum at 460 m $\mu$ . Thus the present experiments were carried out with concentrations of 1.5 mg Ru/l, reversibility was tested and  $\alpha$  was determined as ~3,400. Two samples of the resin (containing 2% or 12% divinylbenzene) were soaked in 3.5 N  $\text{NaNO}_3$  solution and the specific volumes were determined picnometrically with octane resin with 2% divinylbenzene 1.83  $\pm$  0.01 ml/g; with 12% divinylbenzene 1.37  $\pm$  0.01 ml/g. The swelling capacity is doubled in water.

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A057/A129

Determination of the charge of polynuclear....

Since the exchange capacities for both resins are 4.83 - 4.85 mg equiv/g the calculations were done according to equation (3). The concentration of ruthenium in the initial and in equilibrated solutions was determined with a recording CΦ-2M (SF-2M) spectrophotometer and Φ3K-2M (PEK-2M) photoelectrocolorimeter using green filters. From the obtained results (see Fig.) the charge of the complex was calculated with  $z = 5.9$ . Thus data presented by Fletcher et al. are confirmed; on the other hand it is demonstrated that the present method can be used for determinations of the charge of polynuclear complexes. There are: 1 figure and 5 references: 2 Soviet-bloc and 3 non-Soviet-bloc. ✓

SUBMITTED: November 13, 1959

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GRINBERG, A.A.

Theory of the anisotropic photomagnetic effect in germanium.  
Fiz. tver. tela 2 no.1:153-156 Jan '60. (MIRA 14:9)

1. Leningradskiy fiziko-tekhnicheskii institut AN SSSR.  
(Photomagnetic effect) (Germanium)

24392  
S/186/60/002/002/006/022  
E071/E433

21.4200

AUTHORS: Bykhovskiy, D.N. and Grinberg, A.A.

TITLE: Coprecipitation of trivalent cerium with uranium oxalate

PERIODICAL: Radiokhimiya, 1960, Vol.2, No.2, pp.164-174

TEXT: There are many phenomena in the field of coprecipitation of an admixture with a non-isomorphic carrier which are not sufficiently explained. For this reason, the authors investigated the coprecipitation of cerium with uranium oxalate. The determinations of uranium were made by titration with potassium permanganate and of cerium by  $\beta$  activity, using cerium-144 as an indicator. The crystallization experiments were carried out at  $20 \pm 1^\circ\text{C}$ . On precipitation of small quantities of uranium (IV) from the supersaturated solution (20 to 40 mg in 100 ml of solution) in the presence of an excess of oxalic acid, the distribution of cerium between the precipitate and solution corresponded to the logarithmic formula. At a certain excess of oxalic acid, the crystallization coefficient  $\lambda$  remains constant, irrespective of the amount of the carrier precipitated. With an increasing concentration of oxalic acid  $\lambda$  noticeably increases (e.g. with an excess of  $\text{H}_2\text{C}_2\text{O}_4$  of 0.01 M  $\lambda = 1.9$  and

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0.02 M  $\lambda = 2.4$ ). Although the solubility of cerium oxalate under experimental conditions (at a concentration of hydrochloric acid of 1 M and of oxalic acid of 0.01 M the solubility of cerium oxalate is 500 times higher than that of uranium oxalate) was considerably higher than the solubility of uranium oxalate, yet the enrichment of the solid phase by cerium was observed. On coprecipitation of cerium in the absence of an excess of oxalic acid, the crystallization coefficient  $\lambda$  decreases. The influence of pH on  $\lambda$  was investigated within a range of hydrochloric acid concentrations from 0.5 to 3 M. The results indicate that the coprecipitation is governed by the concentration of oxalate ions. The influence of the concentration of cerium on its coprecipitation was studied by means of additions of non-active cerium up to concentrations comparable to the uranium concentration. At low concentrations of cerium (below  $10^{-6}$  M) its coprecipitation is independent of the concentration. At higher concentrations, not exceeding the solubility of cerium oxalate under experimental conditions, crystals with a definite uranium to cerium ratio, independent of their ratio in the solution, are precipitated. The composition of the precipitates obtained at a concentration of

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cerium of  $10^{-3}$  M is characterized by the ratio of  $U:Ce:C_2O_4 = 3.9:1.0:9.5$  which corresponds to the formula  $8U(C_2O_4) \cdot Ce_2(C_2O_4)_3$  (water of crystallization not taken into account). The ratio of uranium to cerium in the precipitate left in contact with the solution steadily increases. Since the coprecipitation of cerium takes place in accordance with the laws of primary adsorption, it was expected that cations which are capable of some interaction with uranium ions should have some influence on the coprecipitation of cerium. The experimental results show that bismuth and calcium salts ( $Bi(NO_3)_3, CaCl_2$ ) lower the coefficient of crystallization ( $\lambda$ ) while other admixtures tested ( $KCl, K_2SO_4, UO_2Cl_2$ ) have a similar influence when present at higher concentrations (0.1 to 0.5 M). On prolonged contact of the crystals obtained by coprecipitation of uranium and cerium with the solution, the return of cerium from the solid phase into the liquid phase is always observed. It is a characteristic feature of the system studied that the approach to equilibrium is attained with great difficulty and, in practice, the mixed crystals are never in equilibrium with the solution. The concentration of cerium in the solution increases with time and does not attain a constant value in five to eight months. The true

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coefficient of crystallization  $D$  is only  $(1-3) \times 10^{-3}$  and the fact that  $\lambda \gg D$  is the main feature of the system which presents difficulties in placing it in the existing classification of coprecipitation processes. There are 1 figure, 10 tables and 16 references: 12 Soviet-bloc and 4 non-Soviet-bloc. The four references to English language publications read as follows:  
H.M.Dawson, Ch.R.Hoskins, J.E.Smith, J.Chem.Soc., 1884 (1929);  
H.M.Dawson, J.E.Smith, J.Chem.Soc., 2530 (1929);  
J.M.Kolthoff, Ch.Rosenblum, J.Am.Chem.Soc., 56, 1658 (1934);  
A.H.Booth, Trans.Farad.Soc., 47, 633 (1951).

SUBMITTED: July 9, 1959

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E071/E433

AUTHORS: Grinberg, A.A. and Mironov, V.Ye.

TITLE: On the exchange of additives in ions  $HgH_4^{2-}$   
( $H^-Cl^-$ ,  $Br^-$ ,  $J^-$ ,  $SCN^-$ )

PERIODICAL: Radiokhimiya, 1960, Vol.2, No.2, pp.249-254

TEXT: It is known that the velocity of exchange of additives in complex compounds of divalent platinum depends mainly on the nature of coordinated groups and noticeably increases in the following series of anions - additives:  $Cl^-$ ,  $Br^-$ ,  $J^-$ ,  $CN^-$ . As the stability of complex ions of the type  $PtX_4^{2-}$  ( $X^-Cl^-$ ,  $Br^-$ ,  $J^-$ ,  $SCN^-$ ,  $CN^-$ ) in the first approximation is similar to that of  $HgX_4^{2-}$ , the authors thought it would be of interest to investigate the exchange in the systems  $HgH_4^{2-} - H^-(H^-Cl^-, Br^-, J^-, SCN^-)$  for which there are no sufficient literature data. The investigation was done using radioactive isotopes of  $Cl^{36}$ ,  $Br^{82}$ ,  $J^{131}$ ,  $S^{35}$ . The experimental procedure was to place a given volume of 0.04 M aqueous solutions of  $K_2 [HgH_4]$  in to one compartment of a flask with a  $\omega$  shaped bottom, and in the other compartment an equal volume of a 0.16 M solution of KH. After obtaining a

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temperature of  $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ , the solutions were mixed in 2 to 3 sec. Immediately after mixing, or after given time intervals, 1.2 to 2 times excess of a precipitant  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ ,  $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$  or  $[\text{Ni}(\text{en})_3]\text{SO}_4$  (en = ethylenediamine) was introduced. The precipitate formed was filtered off, washed to a constant activity of the filtrate and dried at  $80$  to  $90^{\circ}\text{C}$  for 30 to 50 minutes. The activity of the dried precipitates was determined in accurately weighed samples dissolved in appropriate solvents. The experiments were also repeated at  $2^{\circ}\text{C}$  and in the presence of oxidants and using dark vessels. It was found that at  $25^{\circ}\text{C}$  and a  $\text{pH} = 5.6$ , a complete exchange of additives takes place in 3 to 5 sec. Lowering the temperature to  $2^{\circ}\text{C}$  and carrying out the experiments in aqueous alcoholic (50/50) solutions or in the presence of potassium permanganate did not noticeably decrease the velocity of exchange. A high velocity of exchange in all the mercury systems studied did not permit establishing any dependence of the velocity of exchange on the nature of the coordinated groups. It was also found that the solubility of  $[\text{Pt}(\text{NH}_3)_4][\text{HgCl}_4]$  in water at  $25^{\circ}\text{C}$  equals  $2.6 \times 10^{-3}$  mole/l and of  $[\text{Ni}(\text{en})_3][\text{HgCl}_4]$  at Card 2/3.

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18°C is about  $1.2 \times 10^{-2}$  mole/l. There are 2 tables and 7 references: 5 Soviet-bloc and 2 non-Soviet-bloc. The references to English language publications read as follows:  
A.M.Adamson, J.P.Welker, M.Volpe, J.Am.Chem.Soc., 72, 4030 (1950);  
R.L.Rich, H.Taube, J.Phys.Chem., 58, 1, 1 (1954).

SUBMITTED: July 4, 1959

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AUTHORS: Grinberg, A. A., Borzakova, S. S.  
TITLE: On the thiocyanogen ion exchange in  $K_2[Pt(SCN)_4]$  and  $K_2[Pt(SCN)_6]$   
PERIODICAL: Radiokhimiya, v. 2, no. 5, 1960, 574 - 583  
TEXT: The present article submits the data for the exchange reaction in the system:  
$$K_2[Pt(SCN)_4] + 4KS*CN \text{ and } K_2[Pt(SCN)_6] + 6KS*CN.$$

It is pointed out that in the systems investigated by the authors, containing addends with sulfur, there is a strongly defined zero exchange noted. The isotope exchange of thiocyanogen ions in the above-mentioned systems was investigated, depending on the time, concentration of the complex and concentration of the free thiocyanogen ions. The  $K_2[Pt(SCN)_4]$  was prepared from the reaction (Ref. 5: G. B. Buchton, Ann Chem. u. Pharm., 92, 280, 1854):  
$$4KSCN + K_2[PtCl_4] = K_2[Pt(SCN)_4] + 4KCl.$$
 The  $K_2[Pt(SCN)_6]$  was prepared in

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a similar way from the reaction  $6KSCN + K_2[PtCl_6] = K_2[Pt(SCN)_6] + 6KCl$ . The potassium thiocyanogen, labelled with  $S^{35}$  was prepared by melting  $K_4[Fe(CN)_6]$  with sulfur, to which  $S^{35}$  was added (Ref. 6: Yu. V. Karyakin, Chistyie khimicheskiye reaktivy, 192, Goskhimizdat, M. L., 1947). The authors dealt particularly with the question to what extent the exchange between the precipitate and active solution takes place in 5 min. Special experiments were performed to determine the value of the "zero" exchange between the freshly-precipitated non-active precipitates  $[NiEn_3][Pt(SCN)_4]$  and  $[NiEn_3][Pt(SCN)_6]$  and the solutions of the active potassium thiocyanogen in 5 min. The result showed

$$F_0 = \frac{x_{\text{precipitate}}}{x_{\infty}} = 0.31 - 0.34 \text{ (temperature } 20^{\circ}\text{C), for}$$

the  $[NiEn_3][Pt(SCN)_4]$  precipitate, and  $F_0 = 0.30$  for the case of  $[NiEn_3][Pt(SCN)_6]$ .  $F$ , the degree of exchange is said to be the ratio of activity, occurring in the complex for a given period of time ( $x_t$ ), to the activity which should occur in the complex when an equilibrium distribution ( $x_{\infty}$ ) is reached, i.e.,

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$$F = \frac{x_t}{x}$$

The rate of exchange in the thiocyanogen system is said to depend on the illumination. Figure 1 and 2 show graphically the results of the exchange experiments, and Figure 3 shows the relationship of the rate of exchange to the concentration of the complex. The rates of the exchange reactions were calculated from the formula, taking into account the induced exchange (Ref. 7: A. Val', N. Bonner. Ispol'zovaniye radioaktivnosti pri khimicheskikh issledovaniyakh, 12, Izd. IL, M., 1954):

$$R = - \frac{ab}{(a+b)t} [\ln(1-F) - \ln(1-F_0)]$$

where a is the concentration of the complex in g-ions of SCN-/l, b - the concentration of the thiocyanogen ions in g-ions/l. The relationship of the rate of exchange to the concentration of the free thiocyanogen ion is shown graphically in Figure 4. The rates of exchange reactions increase depending on the value of the complex concentration and on the value of the addend  
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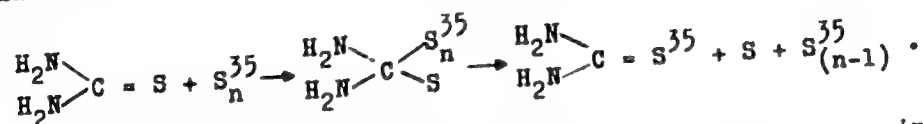
concentration both in the thiocyanogen platinite and in the thiocyanogen platinate systems, thus, the values of the exchange rate constants were calculated from the formula  $R = kC_1^2C_2$ , where  $C_1$  is the concentration of the thiocyanogen platinite in g-ions of  $\text{SCN}^-/1$ , and  $C_2$  - the concentration of the thiocyanogen in g-ions/l, or according to the formula:  $R = kC_1C_2$ , for the thiocyanogen platinate system where  $C_1$  is the concentration of  $\text{K}_2[\text{Pt}(\text{SCN})_6]$  in g-ions  $\text{SCN}^-/1$ , and  $C_2$  - the concentration of  $\text{KSCN}$  in g-ions  $\text{SCN}^-/1$ . In summarizing the results of the experiments the authors bring special notice to the high rate of exchange. The outstanding feature of the system  $[\text{Pt}(\text{SCN})_4]^{2-} + 4\text{S}^*\text{CN}$  (or  $\text{SC}^*\text{N}^-$ ) (Note: \* means  $\text{C}_2\text{H}_5\text{NH}_2$ ), is the high values of the induced exchange, which in turn means in this case, the exchange during the process of the fastest division, i.e., exchange, taking place in the system  $[\text{Pt}(\text{SCN})_4]^{2-} + 4\text{S}^*\text{CN}$  as a result of the addition of  $[\text{NiEn}_3]^{2+}$  or  $[\text{PtEt}_4]^{2+}$  ions, accompanied by actual instantaneous precipitation of  $[\text{NiEn}_3][\text{Pt}(\text{SCN})_4]$  or  $[\text{PtEt}_4][\text{Pt}(\text{SCN})_4]$  residue formation. Special experiments showed that in the given system the exchange of the freshly-precipitated residue with the active solution takes place much more slowly than the induced exchange. The special effect of the precipitating agent cation is even more apparent in the system  $[\text{Pt}(\text{SCN})_6]^{2-} + \text{S}^*\text{CN}^-$ , whereby,

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in this system the cations differ from one another a great deal not only in their rate of exchange of the thiocyanogen ion with the ready precipitates, but in the value of the induced exchange during the process of precipitation. It is further pointed out that the induced exchange in the case of the thiocyanogen platinate system is expressed more weakly than in the thiocyanogen platinite system. The nature of the induced exchange is assumed to be connected to some extent with the ability of the mutual combining of the groups, containing sulfur. A similar combination is expressed in the synthesis process of the labelled sulfur in thiourea, according to the method of Kukhtenko and Mikhluhin (Ref. 11: DAN SSSR, 100, 5, 921, 1955):



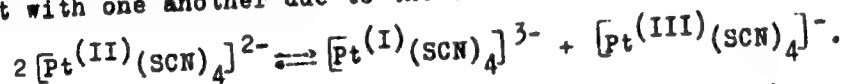
The given data were found to show that the degree of exchange in the system  $[\text{Pt}(\text{SCN})_4]^{2-} + \text{S} \cdot \text{CN}$  increases much more strongly than it should when the relationship to the first degree of concentration of the complex is present (Table 1). Attention is drawn also to the fact that the rate of exchange

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is directly proportional to the second degree of concentration of the free thiocyanogen ion. The first relationship signifies that during the process of the activity occurrence in the complex ion, the exchange of the thiocyanogen ions between two complex ions plays an important role. The second relationship is in accordance with the theory of the intermediary addition of  $\text{SCN}^-$  ions to the  $[\text{Pt}(\text{SCN})_4]^{2-}$  ion. The detected relationships are in accordance with the hypothetical mechanism by which two ions of  $[\text{Pt}(\text{SCN})_4]^{2-}$  interact with one another due to the oxidation-reduction interaction:



Submitted data showed that the nature of the exchange in the system  $[\text{Pt}(\text{SCN})_6]^{2-} + \text{S}^*\text{CN}$  differs greatly from the nature of exchange in the system  $[\text{Pt}(\text{SCN})_4]^{2-} + \text{S}^*\text{CN}^-$ . The period of semi-exchange in the thiocyanogen platinate system is said to be greater than that of the thiocyanogen platinite system. It is pointed out that for the system  $[\text{Pt}(\text{SCN})_6]^{2-}$ , the rate of exchange depends on the complex concentration in the 1.6 degree, and in the concentration of the thiocyanogen ion, it depends on the first degree. It is assumed that an elevated order of the reaction with respect to the complex should be associated with the oxidation-reduction mechanism

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of the exchange. Concluding, the authors state, that they were able to show that the period of semi-exchange T in the system  $[\text{Pt}(\text{SCN})_4]^{2-} + \text{S}^*\text{CN}^-$  (or  $\text{SC}^*\text{N}^-$ ) at a temperature of  $22^\circ\text{C}$ , concentration of the  $\text{K}_2\text{Pt}(\text{SCN})_4$  equal to  $0.5 \cdot 10^{-2}\text{M}$  and concentration of the potassium thiocyanogen  $2 \cdot 10^{-2}\text{M}$ , equals about 6 - 7 min. In the system  $[\text{Pt}(\text{SCN})_6]^{2-} + \text{S}^*\text{CN}^-$ , at a concentration of the complex  $0.5 \cdot 10^{-2}\text{M}$ , the concentration of the  $\text{KS CN}$   $3 \cdot 10^{-2}\text{M}$  and at the same temperature the period of semi-exchange is about 19 min. It was further shown that the rate of exchange in the thiocyanogen platinite system changes proportionately to the second degree of the complex concentration and to the second degree of concentration of the free thiocyanogen ions. In the thiocyanogen platinate system, the rate of exchange depends on the concentration of the free thiocyanogen ions in the first degree, and on the concentration of the complex in the degree 1.6. There are 4 figures and 4 tables, 13 references: 9 Soviet-bloc and 4 non-Soviet-bloc. The four English language publications read as follows: G.B. Buckton, Ann. Chem. u. Pharm. 92, 280, 1854; L. F. Grantham, T. S. Ellman, D. S. Martin, J. Am. Chem. Soc., 77, 11, 2965, 1955; G.W. Watt, R. E. McGarley, J. Am. Chem. Soc., 79, 13, 3315, 1957; G. W. Watt, R. E. McGarley, J. Am. Chem. Soc., 79, 17, 4585, 1957.

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A051/A127

AUTHORS: Grinberg, A. A., Nikol'skaya, L. Ye.

TITLE: Concerning the influence of the solvent on the speed rate of the isotope exchange in complex platinum compounds

PERIODICAL: Radiokhimiya, v. 2, no. 5, 1960, 584-591

TEXT: Referring to the great influence which solvents may have on the speed rate of chemical reactions in general, and on the isotope exchange rate in particular, the authors emphasize that a great number of studies have been made in this field, since labeled atoms could be utilized in this type of experiments. Great attention has been paid to a large group of studies on the exchange between halogen ions and alkyl halogenides. However, the influence of the solvent on the exchange in complex platinum compounds has been investigated very seldom. Regarding this problem, the authors mention a book by F. Basolo and R. G. Pearson (Ref. 4: Mechanism of inorganic reactions. A study of metal complexes in solution. N. Y. 1958), where a so far unpublished study by Wilkins and Lewis on the exchange of

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chlorine in cis- and trans-isomers of  $[\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}_2]$  in acetone is quoted. The Russian scientists, very interested in this type of complexes, investigated the influence of the solvent on the exchange of addenda in  $\text{Pt}(\text{II})$  complexes. Being aware of the great difficulties in a systematic research on this subject, they began to study the exchange problems in the systems  $\text{K}_2[\text{Pt}(\text{SCN})_4] + \text{KSCN}$  in acetone. The exchange kinetics in water for this system has been studied by one of the authors' associate S. S. Borzakova (Ref. 5: Radiokhimiya, 2, 5, 538, 1960). Thus, data on the reactions in these two solvents, i.e. acetone and water may be compared with each other. The experimental part comprises the following main features: It was decided to use for the exchange reaction potassium thiocyanogen, labeled with the isotope  $\text{S}^{35}$ , which has been synthesized by melting of ferrous potassium thiocyanate with sulphur. Acetone was purified, twice distilled after a shake treatment with solid  $\text{KMnO}_4$ ; after another shaking procedure with silver nitrate and sodium hydrate, it was filtered, dried over  $\text{CaSO}_4$  and fractionated during distillation. The acetone solution of  $\text{K}_2[\text{Pt}(\text{SCN})_4]$  and  $\text{KS}^*\text{CN}$  of

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a given (unspecified) concentration were mixed in a centrifuge test tube of a 10-15 ml volume which was closed with a ground stopper and left in the dark for a given (unspecified) period of time. After precipitation of the anion complex, the solution with the precipitate was centrifuged, the precipitate washed and put on a suspended aluminum plate, and its activity was measured with an end-window beta-counter. Special attention had to be paid to the separation after the exchange process. It seemed to be convenient to use the complex cation  $[Pt(NH_3)_4]^{2+}$  as a precipitator for  $[Pt(SCN)_4]^{2-}$ , which in similar experiments with exchanges in aqueous solutions provided for good separation conditions in systems of the type  $[PtX_4]^{2-} + X^-$  (with a not too long exchange period). However, none of the halogenides of the first Reyze base proved to be soluble in acetone. On the other hand, the perchlorate  $[Pt(NH_3)_4](ClO_4)_2$  proved to be soluble, obtained by the authors by adding an additional amount of  $HClO_4$ , which was theoretically required in accordance with the corresponding equation, to the solution of  $[Pt(NH_3)_4](OH)_2$ . Owing to the low solubility in water, the perchlorate I Reyze may be obtained through the reaction of  $HClO_4$  with  $[Pt(NH_3)_4]Cl_2$ . The solubility

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of  $[\text{Pt}(\text{NH}_3)_4](\text{ClO}_4)_2$  in acetone is 0.3 g in 100 ml acetone, and this compound may be used for the precipitation of platinothiocyanide from acetone solutions. A disadvantage in this process is the appearance of  $\text{Pt}(\text{NH}_3)_4(\text{SCN})_2$  which has to be sparged off from the centrifuged precipitate. Precipitation in acetone did not occur instantaneously but took several minutes. Analyses of the precipitate proved that there was no deviation from the basic composition in the precipitated salts. Then, the exchange products were studied as to their dependence on time, the concentration of the complex and the concentration of the addendum, i.e. KSCN, in all cases at 18-19°. For the calculation of the exchange rate over a given period of time, the authors used R. Prestwood's and A. Wahl's (Ref. 9: J. Am. Chem. Soc., 71, 9, 3137, 1949) formula

$$F = \frac{F - F_0}{1 - F_0},$$

which takes into account the zero exchange correction, i.e. the exchange in the separation process and the incomplete separation which have to be considered, too. The zero exchange in the system  $\text{K}_2[\text{Pt}(\text{SCN})_4] + \text{KSCN}$  proved to

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be the same in all experiments. Apparently the dependence of  $1 - F$  on the time (see table 2) by taking into account the zero exchange, expressed in semi-logarithmic coordinates in Figure 1, was found to be a straight line crossing the ordinate axis in a point corresponding to the unit. Thus it is assumed that the rate of the reaction  $R$  abides by the simple exponential law and may be calculated from the formula of simple exchange:

$$R = \frac{-ab}{a+b} \frac{\ln(1-F)}{t}$$

For the concentrations  $0.55 \cdot 10^{-2}$  M (or equally  $2.2 \cdot 10^{-2}$  g-ion.  $\text{SCN}^-/1$ ) in the complex and  $2.2 \cdot 10^{-2}$  M in  $\text{KSCN}$ ,  $R$  was found to be equal to  $0.35 \cdot 10^{-5}$  g-ion.  $\text{SCN}^-/1.\text{min}$ . The period of semi-exchange  $\tau$ , under the given conditions and determined from Figure 1 was found to be equal to 37 hours. For the reaction in water, the same concentrations and temperatures provided, the value  $\tau$  was found to be equal to 6-7 minutes. The tremendous difference in the exchange rate in the two media, with a speed rate of 340 times lower in acetone than in water, as found by S. S. Borzakova (see ref. 5) is assumed to have its origin in a considerable different course of the reaction mechanism which takes place in the two media. Subsequently, the

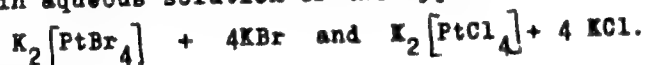
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degree of the dependence on the concentration of the complex in the exchange process has been studied. In these experiments, the concentration of the solution as to KSCN, equal to  $2.2 \cdot 10^{-2}$  M, remained always constant, while the concentration as to  $K_2[Pt(SCN)_4]$  did change. Tabulated data and the curves in Figures 2 and 3, obtained in 50-hr and 25-hr studies showed that the order of the reaction with respect to the complex, determined by the ratio  $\frac{\partial \lg R}{\partial \lg a}$ , is close to the first (1 ~ 1.4). Finally, the degree of

the dependence on the concentration of the addendum has been investigated. The concentration on  $K_2[Pt(SCN)_4]$  in all cases was equal to  $0.55 \cdot 10^{-2}$  M, i.e. to  $2.2 \cdot 10^{-2}$  g-ion  $SCN^-/l$ . The exchange time equaled 25 and 18 hrs. Apparently, a dependence of the exchange rate on the concentration of the addendum was noticed. The order of the reaction with respect to KSCN came also close to the unit, i.e. to the first order. The degree of dependence on the concentration of KSCN is given in Figure 4. Arriving at the conclusions the authors first compare the data of this study with similar systems in aqueous solution of the type



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In accordance with studies made by A. A. Grinberg /the author/ and G. A. Shagisultanova (Ref. 10: Izv. AN SSSR, OKhN, 6, 981, 1955) and by L. F. Grantham, T. S. Elleman and D. S. Martin (Ref. 7: J. Am. Chem. Soc., 77, 10, 2965, 1955), the exchange rate in the above mentioned systems did not depend on the concentration of the addendum, and the exchange chiefly took place through the medium of aqua-ions being formed intermediately. There is no doubt that in this case, i.e. in the study of the authors, a clearly expressed dependence of the exchange rate on the concentration of the addendum does exist, and that, by the same token, there is a difference in the mechanism as compared to that prevailing in the above mentioned systems in aqueous solutions. The tremendous difference in the exchange rates in  $K_2[Pt(SCN)_4]$  when replacing water by acetone as a solvent, primarily may be accredited to the greatly different capabilities of  $H_2O$  and  $CH_3COCH_3$  molecules to penetrate into the interior sphere of the  $[Pt(SCN)_4]^{2-}$  ion, and also to the differing dielectric constant values. Of considerable interest is the practical identity of the absorption spectra of the two complexes  $K_2[Pt(SCN)_4]$  and  $[Pt(NH_3)_4][Pt(SCN)_4]$ . In this given case and in

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A051/A127

Concerning the influence of the solvent...

the solid state no anomalous colorations of the Magnus and Beelman type salts have been noted. The relatively difficult solubility of the perchlorate of the first Reye base in water deserves special attention, since one may assume that the perchlorate ions might prove useful as precipitants for some other bivalent complex ions of the tetramine type, in connection with the already known reaction with cadmium resulting in the formation of a difficultly soluble product of the composition:

$$[\text{Cd}(\text{NH}_3)_4](\text{ClO}_4)_2$$

Card 8/10

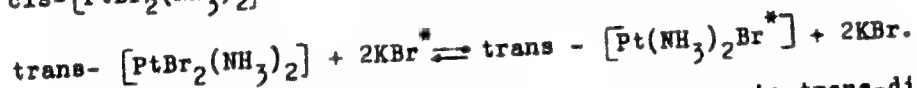
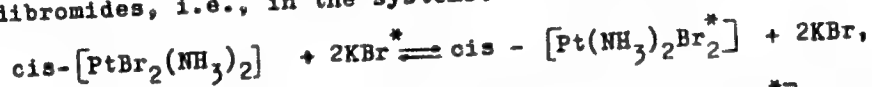
S/186/60/002/005/011/017  
A051/A130

AUTHORS: Grinberg, A. A.; Shagisultanova, G. A.

TITLE: The substitution of bromine in cis-trans-diammindibromide bi-valent platinum.

PERIODICAL: Radiokhimiya, v. 2, no. 5, 1960, 592 - 595

TEXT: A study was made of the substitution reactions in cis-trans-diammindibromides, i.e., in the systems:



It was shown that the bromine ion exchange in the system cis-trans-diammindibromide platinum-potassium bromoplatinite takes place rapidly. It is assumed that the rapid exchange is determined by the migration phenomena of the bromine from one internal sphere to another. The above-mentioned sys-

Card 1/6

S/186/60/002/005/011/017  
A051/A130

The substitution of bromine in ....

tem is said to be convenient to investigate since the reacting components are easily separated by precipitation of the green salt of Biil'man (Beelman ?)  $[\text{Pt}(\text{NH}_3)_4][\text{PtBr}_4]$ . The exchange of the bromine ions was found to take place even more rapidly when, under the same conditions trans-diammin and  $\text{K}_2[\text{PtBr}_4]$  are taken. Tables 1 and 2 show that even at very low concentration of the diammines and a correspondingly low concentration of  $\text{K}_2[\text{PtBr}_4]$ , the bromine exchange takes place rapidly, rendering the study of the exchange kinetics in the trans-salt impossible. The experimental procedures used were those described in Ref. 1 and 2 (A. A. Grinberg, G. A. Shagisultanova, Izv. AN SSSR, OKhN, 6, 981, 1955; A. A. Grinberg, G. A. Shagisultanova, Radiokhimiya, 7, 1, 91, 1959). A determination of the values of the induced exchange showed that these differ significantly in the two cases investigated, i.e., for the system cis- $[\text{PtBr}_2(\text{NH}_3)_2] + \text{K}_2 \text{PtBr}_4$ , where it did not exceed 4%, and the system trans- $[\text{PtBr}_2(\text{NH}_3)_2] + \text{K}_2[\text{PtBr}_4]$ , where it fluctuated between 8 and 11%. The data of tables 1 and 2, with a correction added for zero exchange, lead to the conclusion that the period of semi-exchange for the first system at  $C_{\text{PtBr}_2(\text{NH}_3)_2} = 0.26 \cdot 10^{-3} \text{M}$ ,

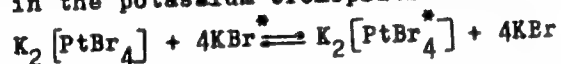
$C_{\text{K}_2\text{PtBr}_4} = 0.34 \cdot 10^{-3} \text{M}$  and  $t^0 = 25^\circ\text{C}$ , is approximately equal to 60 min.

Card 2/6

S/186/60/002/005/011/017  
AO51/A130

The substitution of bromine in ....

the period of semi-exchange for the second system in the same concentrations and temperature conditions - the order of 10 - 12 min. Thus, the bromine in the trans-diammine exchanges much faster than in the cis-diammindibromide, and the bromine in the diammines exchanges much faster than the bromine in the potassium bromoplatinite in the system



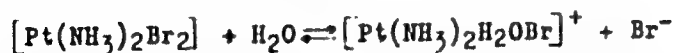
for which  $T_{\frac{1}{2}} = 120$  minutes at  $C_{K_2PtBr_4} = 0.55 \cdot 10^{-2}$  M and  $t^{\circ}C = 20^{\circ}C$ .

Experiments for reverse exchange in the same systems showed that the results were the same as in the previous case (Table 1 and 2). Experimental results also confirmed the previous observations on the rapidity of the bromine exchange between the complex ions. The authors point out that the exchange between the complex ions, containing the coordinated bromine ions takes place much more rapidly than between the  $[PtBr_4]^{2-}$  ions and the free bromine ions. Another fact brought to light is the atom exchange of bromine between the trans- $Pt(NH_3)_2 - Br_2$  and  $[PtBr_4]^{2-}$ , which takes place faster than in the case of the cis-isomer. The observed phenomena are explained by the reaction of the type:

Card 3/6

S/186/60/002/005/011/017  
A051/A130

The substitution of bromine in ....



with subsequent mutual attraction of the oppositely-charged complex ions  $[\text{Pt}(\text{NH}_3)_2\text{H}_2\text{OBr}]^+$ ,  $[\text{PtBr}_4]^{2-}$  and  $[\text{PtBr}_3\text{H}_2\text{O}]^-$ . Ion-pairs are formed of the  $[\text{Pt}(\text{NH}_3)_2\text{H}_2\text{OBr}][\text{PtBr}_4]^-$  type and correspondingly:  $[\text{Pt}(\text{NH}_3)_2\text{H}_2\text{OBr}][\text{PtBr}_4]^-$ .

The rapid exchange observed by the authors between the complex ions as compared with the exchange rate in the system  $[\text{PtBr}_4]^{2-}$  + free bromine ions help to understand the information discussed in Ref. 2, concerning the presence of the second order reaction for the complex in the system  $[\text{Pt}(\text{NH}_3)_2\text{Br}_2] + 3 \text{KBr}^+$ , and order above one for  $[\text{PtBr}_4]^{2-} + 4\text{KBr}^+$ . There are two tables and 6 references: 4 Soviet block and 2 non-Soviet-bloc. The English language publications read as follows: D. Banerjee, F. Basolo, R. Pearson, J. Am. Chem. Soc. 79, 4055, 1957; F. A. Long, J. Am. Chem. Soc., 73, 3537, 1939.

Card 4/6



BYKHOVSKIY, D.N.; GRINBERG, A.A.

Coprecipitation of trivalent cerium with uranium oxalate.  
Radiokhimiia 2 no.6:164-174 '60. (MIRA 14:4)  
(Cerium) (Uranium oxalate)

GRINBERG, A.A.; MIRONOV, V. Ye.

Exchange of addends in  $\text{Hg} \Gamma_4^{2-}$  ions. Radiokhimiia 2 no.6:249-254  
'60. (MIRA 14:4)

(Mercury compounds)

24086

3/186/60/002/006/010/026

A051/A129

21 4200

AUTHORS: Grinberg, A.A., Vykhovskiy, D. N., Nikol'skiy, L. Ye.;  
Petrzhak, G.I.

TITLE: The formation of tetra-valent uranium oxalate from solutions  
using rongalite

PERIODICAL: Radiokhimiya, v. 2, no. 6. 1960, 687 - 690

TEXT: The authors have established the conditions of precipitation of uranium (IV) oxalate, resulting from the determination of the losses of tetra- and hexa-valent uranium in filtrates, using rongalite. It is shown that in the formation of low quantities of uranium the rongalite concentration in the solution should not be below 0.1 M. Experiments were conducted to establish the uranium losses in the filtrates after the formation of tetra-valent uranium oxalate. The results obtained show that at the given concentrations about 40 mg of uranium are left in the solution, whereby the losses seem to be connected with an increased solubility of the tetra-valent uranium oxalate in the filtrates. The experiments carried out for establishing the conditions of low-quantity formations of uranium showed that at low concentrations of uranium in

Cont 1/3

24056

S/186/60/002/006/010/026  
A051/A129

The formation of tetra-valent ....

the solution the rongalite content had to be increased as compared to the theoretically computed quantity. The deviation of the stoichiometry under these conditions is said to be due to the low rate of uranium reduction and the strong effect of the side reactions taking place at the same time. Further experiments were conducted to check the uranium losses resulting from the addition of small quantities of rongalite to the uranium solution already reduced which noticeably increase due to oxidation of uranium. Rongalite was added to a hydrochloric acid solution of tetra-valent uranium. The results showed that the amount of uranium formed in this case was always less than in similar experiments without rongalite and decreased with time. The quantity of tetra-valent uranium in oxalate residues was determined with an accuracy of 0.1 mg by dissolving the residue in sulfuric acid and titrating it with potassium permanganate. Normal oxalate was obtained in each case at a ratio of

$\frac{C_2O_4}{U} = 2$ . The quantity of oxidized uranium was determined from the difference, correcting for solubility. The oxidation of uranium in the third series of experiments is thought to take place as a result of certain intermediate compounds formed in the interaction of rongalite and air oxygen. When large quantities

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24086

S/186/60/002/006/010/026  
A051/A129

The formation of tetra-valent ....

of ronalite are present, this phenomenon does not occur. There are 3 tables and 4 references: 3 are Soviet-bloc and 1 non-Soviet-bloc. The reference to the English language publication reads as follows: W. H. Reas. The Transuradium Elements, 423, N.Y., 1949.

SUBMITTED: October 26, 1959.

Card 3/3

68221

S/078/60/005/02/007/045  
B004/B016

5(2) 5.2620

AUTHORS: Grinberg, A. A.  
Shagisultanova, G. A.

TITLE: Stability of Complex Compounds of Bivalent Platinum<sup>1</sup>

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol 5, Nr 2, pp 260-262 (USSR)

ABSTRACT: The authors point out that there are only few data available in publications concerning the instability constants of typical complex compounds of bivalent Pt. They quote in this connection a paper by I. I. Chernyayev and S. I. Khorunzhenkov. Since many problems arose when investigating reactions of the isotopic exchange (Refs 4,5) and substitution (Ref 6), the authors determined the instability constants of the following processes:  $[PtCl_4]^{2-} + H_2O \rightleftharpoons [PtCl_3H_2O]^{-} + Cl^{-}$ ;  $[PtNH_3Cl_3]^{-} + H_2O \rightleftharpoons [PtNH_3H_2OCl_2]^{0} + Cl^{-}$ ; cis- (or trans-)  $[Pt(NH_3)_2Cl_2] + H_2O \rightleftharpoons$  cis- (or trans-)  $[Pt(NH_3)_2H_2OCl]^{+} + Cl^{-}$ , and  $[PtBr_4]^{2-} + H_2O \rightleftharpoons [PtBr_3H_2O]^{-} + Br^{-}$ . The authors added to the freshly prepared diluted solutions of the complex compounds

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68221

S/O/6/60/005/02/001/045  
B004/B016

Stability of Complex Compounds of Bivalent  
Platinum

varied quantities of KCl (or KBr), allowed the solutions to stand in the dark until equilibrium was established, and then determined the content of aquo ions and the equilibrium concentration of the unchanged complex ion. The equilibrium concentration of the chlorine- (or bromine-) ion equaled the concentration of the halogen salt added plus the concentration of aquo ions. The calculation of the instability constant is given for the example  $K_2[PtCl_4]$  (Table 1). In table 2, the spread of

the experimental values of the instability constants of  $K[PtNH_3Cl_3]$  is shown. The authors found the following:

1)  $K_2[PtBr_4]$  is more stable than  $K_2[PtCl_4]$ ; 2) on transition from  $K_2[PtCl_4]$  to  $[Pt(NH_3)_2Cl_2]$ , the instability constants

which correspond to the separation of one chlorine ion, decrease with increasing substitution of  $NH_3$  for the chlorine atoms; 3) the instability constant of the reaction

$[Pt(NH_3)_2Cl_2] + H_2O \rightleftharpoons [Pt(NH_3)_2ClH_2O]^+ + Cl^-$  is considerably smaller in the trans-isomer than in the cis-isomer. The resultant instability constants have an order of magnitude of

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-8221

Stability of Complex Compounds of Bivalent  
Platinum

S/076/60/005/02/007/045  
B004/B016

$10^{-2}$ . The authors now investigate the problem as to whether the results obtained may be extended to compounds of bivalent Pt, in which Br, J or acid radicals are substituted for Cl. Briefly mentioned are attempts to titrate solutions of  $K_2PtCl_4$  without addition of KCl, in which connection also a substitution of the second chlorine ion by  $H_2O$  was observed. There are 2 tables and 6 references, 5 of which are Soviet. 4

SUBMITTED: November 20, 1958

Card 3/3



69052

5.2620  
AUTHORS:

Grinberg, A. A., Snikhayeva, L. V.

S/078/60/005/03/016/048  
B004/B002

TITLE:

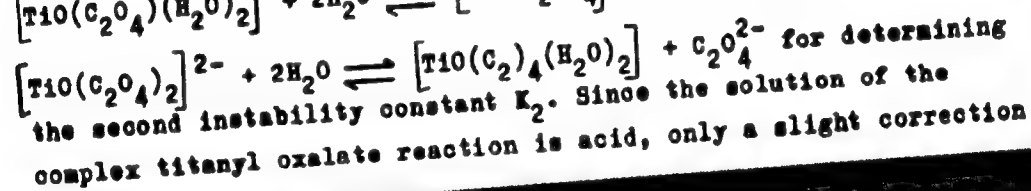
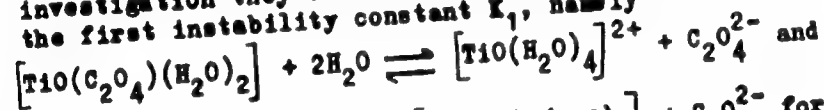
The Stability of Complex Titanyloxalate in Solutions

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1960, Vol 5, Nr 3, pp 599-603 (USSR)

ABSTRACT:

The authors refer to a paper by B. V. Ptitsyn and L. I. Vinogradova (Ref 1) who determined the instability constant of  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  by means of an oxalate-silver electrode, and state the reasons for having chosen an oxalate-mercury electrode. The instability constant of  $[\text{TiO}(\text{C}_2\text{O}_4)_2]^{2-}$  was determined by means of a potentiometric titration with HCl and by determining the oxalate ion by means of an oxalate-mercury electrode. The authors specify the six equilibria existing in the solution of potassium titanyl oxalate. In their investigation they chose the following equilibria for determining the first instability constant  $K_1$ , namely



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69052

The Stability of Complex Titanyloxalate in Solutions

S/078/60/005/03/016/048  
B004/B002

of the instability constant is necessary. Experimental data are given in table 1. Table 2 gives the concentrations calculated for the complexes and the  $C_2O_4^{2-}$  ions, and also the values of  $K_2$ . The mean value found was  $K_2 = 0.77 \cdot 10^{-5}$ . The values obtained by potentiometric titration with HCl, were examined by means of an oxalate-mercury electrode. Calibration of the electrode by means of potassium oxalate is described. Experimental results are shown in table 3. Table 4 gives the concentrations and values computed as to  $K_2$ .  $K_2 = 4.1 \cdot 10^{-5}$ . The determination of  $K_1$  was made indirectly on the basis of the general instability constant  $K_{gen}$  which by means of potentiometric titration with lye according to Bose (Ref 5), was found to be  $1.5 \cdot 10^{-15}$ . Hence,  $K_1$  was computed to be  $2 \cdot 10^{-10}$ . A. K. Babko and L. I. Dubovenko (Ref 6) spectrophotometrically determined  $K_1$  to be  $1.5 \cdot 10^{-7}$ . These values are to be better defined by further investigations. There are 4 tables and 9 references, 6 of which are Soviet.

SUBMITTED:  
Card 2/2

November 25, 1958

GRINBERG, A.A.; LOZHKINA, G.S.

Extraction of acids with organic solvents. Zhur. neorg.khim. 5  
no.3:738-744 Mr '60. (MIRA 14:6)

(Acids, Inorganic)  
(Extraction (Chemistry))

S/078/60/005/06/29/030  
BC04/B014

5.2400  
5.2100(B)  
AUTHORS: Grinberg, A. A., V'yugina, A. F.

TITLE: Interaction Between Nitric Acid and Magnesium

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 6,  
pp. 1389 - 1390

TEXT: The present paper is intended to check a paper by C. Montemartini (Ref. 1) concerning the composition of gases formed by interaction between  $\text{HNO}_3$  and Mg. Pure MA1 (MA1) magnesium (analysis is given) was boiled with chemically pure  $\text{HNO}_3$  in a vessel with a reflux condenser. The gases were collected under a saturated NaCl solution, and analyzed for  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{H}_2$  in a BTM(VTI) apparatus. The free  $\text{HNO}_3$  and  $\text{NH}_3$  was also determined in the solution. Hydroxylamine could not be detected. Experimental results are given in Figs. 1 and 2. The quantity of released  $\text{H}_2$  decreases with increasing  $\text{HNO}_3$  : Mg ratio. The largest quantity of  $\text{H}_2$  is

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Interaction Between Nitric Acid and Magnesium S/078/60/005/06/29/030  
B004/B014

160 g per 1 g of Mg. These gases are explosive because of their high  $H_2$  contents (6 - 32%). Their nitrogen contents were always lower than 75%. When the concentration of  $HNO_3$  varied between 0.1 and 3 N, and the  $HNO_3$  : Mg ratio between 1 : 1 and 10 : 1, a fraction of 0.4 molecule of  $HNO_3$  was always consumed for 1 Mg atom to form the individual reaction products. Though the reaction kinetics was not studied, the authors believe that the reaction products containing more than one nitrogen atom are formed by secondary processes, such as  $NH_4NO_2 \rightarrow N_2 + 2H_2O$ . The authors refer to papers by D. I. Mendeleyev (Ref. 2), B. N. Menshutkin (Ref. 3), and B. V. Nekrasov (Ref. 4). There are 2 figures and 7 references: 4 Soviet, 1 British, and 1 Italian.

SUBMITTED: December 15, 1958

Card 2/2

GRINBERG, A.A.; SHAGISULTANOVA, G.A.

Instability constants of bromide complexes of divalent platinum.  
Zhur. neorg. khim. 5 no.8:1895 Ag '60. (MIRA 13:9)  
(Platinum compounds)

S/020/60/132/05/27/069  
B011/B126

AUTHORS: Grinberg, A. A., Academician, Kukushkin, Yu. N.  
TITLE: The Hydrolysis Kinetics of Some Complex Compounds of Pt (IV)  
PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 5, pp. 1071 - 1073

TEXT: The object of this paper is to study the hydrolysis kinetics of the following complexes:  $\text{Na}_2[\text{PtCl}_6]$ ,  $\text{k}[\text{PtNH}_3\text{Cl}_5]$ ,  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ ,  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$ ,  $\text{trans}-[\text{Pt}(\text{NH}_3)_4\text{Cl}_2](\text{NO}_3)_2$ ,  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ , and  $\text{k}[\text{PtPyCl}_5]$  (Py - pyridine). Hitherto only the isomeric diammines of this series have not been investigated. In their experiments, carried out in darkness, the authors used red-lacquered receptacles. The experiments showed the expected variety in the hydrolysis kinetics of single members of this series. The dependence of the hydrolysis rate on alkali concentration is expressed in  $\text{k}[\text{PtNH}_3\text{Cl}_5]$  and  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2](\text{NO}_3)_2$  and also

Card 1/2

The Hydrolysis Kinetics of Some Complex  
Compounds of Pt (IV)

S/020/60/132/05/27/069  
B011/B126

with a certain approximation in  $[Pt(NH_3)_5Cl]Cl_3$  by an equation of the first order. The hydrolysis rate is independent of the alkali concentration for triamine and pyridine compounds. These compounds are reduced during hydrolysis to compounds of Pt (II), as against the unusually high hydrolysis rate of mono-, tri-, and tetramine with respect to the concentration of the complex. When temperature is raised, the reduction is greater. Chloroplatinate, pyridine monoamine, and pentamine were not even reduced by alkali on heating under the conditions of the experiment. The authors give a scheme of the hydrolysis reaction, and state that the mechanism of the hydrolysis of  $trans-[Pt en_2Cl_2]^+2$

does not reflect the process taking place in the solution. The mechanism of the interaction of this compound with alkali is much more complicated. Corresponding investigations are about to be completed, and the results will soon be published. The authors refer to papers by O.Ye. Zvyagintsev and Ye.F. Karandasheva (Ref. 1). There are 9 references: 5 Soviet and 4 American.

*Radium Inst. im V.G. Khlopin, AS USSR* ✓

Card 2/2



GRINBERG, A.A., akademik; GEL'FMAN, M.I.

Stability of complex compounds of divalent platinum. Dokl. AN SSSR  
133 no.5:1081-1083 Ag '60. (MIRA 13:8)

1. Leningradskiy tekhnologicheskii institut im. Lensovetu.  
(Platinum compounds)

31886

S/186/61/003/005/003/022

E071/E485

21.4300

AUTHORS: Grinberg, A.A. and Bykhovskiy, D.N.

TITLE: Coprecipitation of microquantities of thorium  
(uranium X<sub>1</sub>) with uranium oxalate

PERIODICAL: Radiokhimiya, v.3, no.5, 1961, 528-534

TEXT: Since oxalates of thorium and tetravalent uranium are isomorphic and ions of U<sup>4+</sup> and Th<sup>4+</sup> are close in their dimensions, an isomorphic coprecipitation should take place in this system. The authors studied this coprecipitation process under various crystallization conditions in order to find out how the process could be utilized for the separation of the thorium isotope uranium X<sub>1</sub> from uranium salts. It was also intended to compare the behaviour of an isomorphic admixture with a non-isomorphic one, e.g. with the coprecipitation of trivalent cerium with uranium oxalate which was studied previously (Ref.5: D.N.Bykhovskiy, A.A.Grinberg, Radiokhimiya, v 2. 2. 164 (1960)). The experimental procedure was the same as in the abovementioned work. It was found that on precipitation of uranium X<sub>1</sub> with uranium oxalate from a supersaturated solution the distribution of uranium X<sub>1</sub>

X

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31586  
S/186/61/003/005/003/022  
E071/E485

Coprecipitation of microquantities ...

corresponds to the logarithmic formula. The coefficient of distribution  $\lambda$  increases with increasing concentration of oxalate ions. The isomorphic system  $UX_1(C_2O_4)_2 - U(C_2O_4)_2$  differs from the non-isomorphic  $Ca^{III} - U(C_2O_4)_2$  system in its stability of the mixed crystals formed. Since  $UX_1$  coprecipitates with uranium oxalate (IV) with an enrichment of the solid phase, its quantitative separation can be achieved on precipitation of small quantities of uranium (IV). By precipitating  $UX_1$  in the form of oxalate with some uranium (IV) it can be separated from the main mass of uranium present in the six valent state. Preliminary synthesized oxalate can be used as a source of the tetravalent uranium. In the dry state, this salt can be stored. The necessary amount of uranium oxalate can be dissolved on heating in an aqueous solution of either potassium or ammonium oxalate (2 moles of  $K_2C_2O_4$  or  $(NH_4)_2C_2O_4$  per 1 mole of  $U(C_2O_4)_2$ ). The other method is to reduce with ronalite a small amount of six valent uranium present in the solution from which  $UX_1$  is to be separated. The best results were obtained when the initial concentration of uranium (IV) was about 30 g/litre, under these conditions an enrichment by a factor of 100 is obtained with practically complete

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S/186/61/003/005/003/022

Coprecipitation of microquantities . . E071/E485

separation of  $UX_1$ . The presence of a large quantity of uranyl makes the precipitation of tetravalent uranium oxalate difficult. In such cases, it is advantageous to first precipitate uranyl oxalate and then from the filtrate, containing a small quantity of uranium and practically the whole  $UX_1$ , separate  $UX_1$  with oxalate of tetravalent uranium. By repeating the process, the necessary degree of enrichment in  $UX_1$  can be obtained. The subsequent separation of  $UX_1$  from uranium can be done using an iron exchange resin. The authors used cationite Yy-2 (KU-2). Thus a method of separation of uranium  $X_1$  from uranium based on the ability of uranium  $X_1$  to coprecipitate with uranium oxalate and not to coprecipitate with uranyl oxalate was developed. It is claimed that this method can compete with the ether extraction normally used for this purpose. There are 5 tables and 10 references: 5 Soviet-bloc, 1 a Russian translation from non-Soviet-bloc publication and 4 non-Soviet-bloc. The three references to English language publications read as follows:

- Ref. 3. A.H. Booth, J. Chem. Educ., v. 28, 3, 144 (1951),  
 Ref. 4. A.E. Taylor, P.T. Dillon, Anal. Chem., v. 24, 10, 1624 (1952);  
 Ref. 6. M. Bose, D.M. Chowdhury, J. Indian Chem. Soc., v. 31, 2, 111  
 Card 3/4 <sup>3</sup> (1954). X

GRINBERG, A.A.; SHAGISULTANOVA, G.A.

Exchange of bromine in potassium monopyridinetribromoplateate.  
Radiokhimiia 3 no.6:694-700 '61. (MIRA 14:12)

(Bromine)  
(Platinum compounds)

SHIMONEG, A.A.; GIL'DENGAS'IL', Kh.I.; SIBL'SKAYA, V.V.

Mixed methylamine-ammonia platinum pentam ine and its acidic pro-  
perties. Zhur. neorg. Khim. 6 no.1:90-94 '61. (M.A 14:2)  
(Platinum compounds)

GRINBERG, A.A.; SLOBODSKAYA, D...

Kinetics of the reactions between platinumites and amines. Zhur. neorg.  
khim. 6 no.1:99-102 '61. (MIRA 14:2)  
(Amines) (Potassium bromoplatinate)  
(Potassium chloroplatinate)

GAINBERG, A.A.; SHOLETSKAYA, D.B.

Kinetics of the interaction of amines with Cos. type salts. Zhur.  
neorg. khim. 6 no.1:103-110 '61. (II A 1/12)  
(Amines) (Platinum compounds)



GRINBERG, A.A.; STETS, N. A.I.

Acid-base properties of cis and trans isomers of  $[Pt(NH_3)(NH_2OH)_2]Cl_2$ .  
Zhur. neor. khim. 6 no.1:111-119 no.1: '61. (2:2 A 14:1)  
(Platinum compounds)

GRINBERG, A.A.; KHAKIMOV, Kh.Kh.

Stability constants of cobalt complexes with certain vitamins. Zhur.  
neorg. khim. 6 no.1:14-152 '61. (MIRA 14:2)  
(Cobalt compounds)

S/078/61/006/002/003/017  
B017/B054

AUTHORS: Grinberg, A. A., Astapovich, V. I.  
TITLE: Study of Oxalic Acid Complex Compounds of Zirconium  
PERIODICAL: Zhurnal neorganicheskoy khimii, 1961, Vol. 6, No. 2,  
pp. 321 - 329

TEXT: To separate zirconium and hafnium, the oxalate complexes of these elements have recently been studied in detail (Ref. 8). A. N. Yermakov, V. K. Belyayeva, and I. N. Marov (Ref. 9) studied the possibilities of separating zirconium and hafnium by ion exchangers with the aid of oxalate complexes. V. F. Saksin (Ref. 11) studied the zirconyl oxalate complexes. In the present paper, the authors checked the conditions of producing simple and complex zirconium oxalates. The following compounds were produced:  $ZrOC_2O_4 \cdot nH_2O$ ,  $Zr(C_2O_4)_2 \cdot nH_2O$ , and  $K_4Zr(C_2O_4)_4 \cdot 4H_2O$ . Some physico-chemical properties of zirconium oxalate and potassium zirconium oxalate were studied; results are given in Tables 1 and 2. The calcium, barium, cadmium, and lead salts were synthesized by exchange of the potassium ion

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Study of Oxalic Acid Complex Compounds  
of Zirconium

S/078/61/006/002/003/017  
B017/B054

in the potassium zirconium oxalate complex. The chemical formulas of these compounds are as follows:  $\text{Ca}_2[\text{Zr}(\text{C}_2\text{O}_4)_4] \cdot 5.5\text{H}_2\text{O}$ ,  $\text{Ba}_2[\text{Zr}(\text{C}_2\text{O}_4)_4] \cdot 7\text{H}_2\text{O}$ ,  $\text{K}_2\text{Cd}[\text{Zr}(\text{C}_2\text{O}_4)_4] \cdot 5.4\text{H}_2\text{O}$ , and  $\text{Pb}_2[\text{Zr}(\text{C}_2\text{O}_4)_4] \cdot 3\text{H}_2\text{O}$ . The stability constant of the zirconium oxalate complex was determined; results are given in Table 3.  $K_H$  was found to be  $10^{-4}$ . There are 3 tables and 13 references: 5 Soviet, 2 US, 3 French, and 3 German. ✓

Card 2/6  
✓

GRINBERG, A.A.; KUKUSHKIN, Yu.N.

Hydrolysis kinetics of some complex compounds of tetravalent platinum.  
Zhur.neorg.khim. 6 no.5:1084-1097 My '61. (MIRA 14:4)

(Platinum compounds)

GRINBERG, A.A.; NIKOL'SKAYA, L.Ye.; SHAGISULTANOVA, G.A.

Chromatographic method for determining the structure of  
coordination polymer compounds. Zhur. neorg. khim. 6 no.7:  
1497-1500 J1 '61. (MIRA 14:7)  
(Platinum compounds) (Ammonia)

GRINBERG, A. A.

Present state and prospects of the development of coordinative chemistry. *Analele chimie* 16 no.4:45-55 Q-D '61.

(Chemistry)

GRINBERG, A.A., akademik; STETSENKO, A.I.; IN'KOVA, Ye.N.

Acidic properties of cis- and trans-isomers of  $[\text{Pt}(\text{glu})_2(\text{NH}_3)_2] \text{Cl}_2$ .  
Dokl. AN SSSR 136 no.4:821-823 P '61. (MIRA 14:1)

1. Leningradskiy tekhnologicheskii institut imeni Lensoвета.  
(Platinum compounds)



GRUBBS, A.A., akademik; SEL'FAN, I.I.

Stability of complex compounds of divalent platinum. Compounds  
of the tetraamino type. Dokl. Ak. Nauk SSSR 157 no. 1:67-69 1964 p 61.  
(Chem. 17:2)

1. Leningradskiy tekhnologicheskii institut im. Lensoyeta.  
(Platinum compounds)

GRINBERG, A.A., akademik; GEL'FMAN, M.I.; IN'KOVA, Ye.N.; SHAGISULTANOVA, G.A.

Presence of exchange between irradiated metallic platinum and complex  
ions of divalent platinum in aqueous solutions. Dokl. AN SSSR 137  
no.3:597-598 Mr '62. (MIRA 14:2)

(Platinum--Isotopes)

GRINBERG, A.A., akademik; KUKUSHKIN, Yu.N.

Interaction between alkali and trans-(Pt<sub>2</sub>Cl<sub>2</sub>)Cl<sub>2</sub>.  
Dokl. AN SSSR 140 no.5:1076-1078 O '61. (MIRA 15:2)

1. Radiyevyy institut im. V.G.Khlopina AN SSSR.  
(Platinum compounds)  
(Alkalies)

S/186/62/004/003/006/022  
EO71/E433

AUTHORS: Grinberg, A.A., Petrzhak, G.I., Lozhkina, G.S.

TITLE: Some new salts of uranyloxalic acid

PERIODICAL: Radiokhimiya, v.4, no.3, 1962, 289-295

TEXT: The authors investigated the synthesis of salts of uranyloxalic acid with complex cations. Initially it was attempted to obtain compounds with cations  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$  and anion  $[\text{U}(\text{C}_2\text{O}_4)_4]^{4-}$  by the double exchange reaction in a neutral medium. However, these compounds were not isolated, due to their rapid decomposition caused by the oxidizing-reducing interaction between the components of the complex formed. Subsequently the reaction between chromium-hexacarbamide chloride (III) and potassium uranyloxalate was tried. A new complex compound chromium hexacarbamide uraneate  $[\text{Cr}(\text{N}_2\text{H}_4\text{CO})_6]_4[\text{U}(\text{C}_2\text{O}_4)_4]_3 \cdot 11\text{H}_2\text{O}$ , in which the anion of uranyloxalic acid is bound to trivalent complex chromium cation, was synthesized. It was shown that this compound is stable in air and can be obtained either with an excess of  $\text{K}_4[\text{U}(\text{C}_2\text{O}_4)_6]_4$  or of  $[\text{Cr}(\text{N}_2\text{H}_4\text{CO})_6]\text{Cl}_3$ . The compound is little soluble in water (30 mg per litre) and

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Some new salts of ...

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diluted mineral acids. On heating it is soluble in nitric (1:1), hydrochloric (1:1) and sulphuric (1:20) acids. It is practically insoluble in ether, alcohol, benzene, carbon tetrachloride, isoamylacetate and isoamylalcohol. The solubility was determined by synthesizing the compound labelled with uranium-233. It was found that during dissolving in water a partial oxidation of  $U^{(IV)}$  into  $U^{(VI)}$  takes place. There are 5 tables.

SUBMITTED: April 7, 1961

Card 2/2

GRINBERG, A.A.; IN'KOVA, Ye.N.; DOBROBORSKAYA, A.I.

Solubility of geometrical isomers of platinum complexes in  
solutions of electrolytes. Zhur.neorg.khim. 7 no.5:987-991  
My '62. (MIRA 15:7)  
(Platinum compounds) (Solubility)

GRINBERG, A.A.; GEL'FMAN, M.I.

Interaction of complex compounds of the same metal in the same  
oxidation state. Zhur.neorg.khim. 7 no.5:992-996 My '62.

(Complex compounds)

(MIRA 15:7)

GRINBERG, A.A.; YUAN' KAN [Yuan K'ang]

Complex compounds of tetravalent platinum with glycol. Zhur.  
neorg.khim. 7 no.10:2304-2310 0 '62. . (MIRA 15:10)  
(Platinum compounds) (Ethylene glycol)



GRINBERG, A.A.; SHAGISULTANOVA, G.A.

Instability constants of platinum complexes. Zhur.neorg.khim.  
7 no.10:2311-2314 0 '62. (MIRA 15:10)  
(Platinum compounds)

GRINBERG, A.A.; STETSENKO, A.I.

Acidic properties of cis- and trans-isomers of  $[\text{Pt}(\text{NH}_2\text{OH})_2(\text{Py})_2]\text{Cl}_2$ .  
Zhur.neorg.khim. 7 no.12:2678-2684 D '62. (MIRA 16:2)  
(Platinum compounds) (Isomerization)

GRINBERG, A.A., akademik; KUZ'MINA, M.A.

Isotopic exchange of chlorine in Zeise's salt. Dokl. AN SSSR  
144 no. 4: 798-801 Je '62. (MIRA 15:5)  
(Chlorine—Isotopes) (Platinum compounds)

GRINBERG, A.A., akademik; KUKUSHKIN, Yu.N.

On the existence of ammoniated salts of quadrivalent platinum.  
Dokl.AN SSSR 145 no.1:97-99 J1 '62. (MIRA 15:7)  
(Platinum compounds) (Amines)